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(57) Abstract

It has been discovered that metal-containing components can be transferred from a hydrocarbon phase to a water phase in an emulsion breaking process by using a composition which is a blend of polymers. The composition includes at least one diepoxide polymer, at least one polyol; and preferably at least one aromatic sulfonic acid. An aromatic solvent may be optionally included in the composition. The invention permits transfer of metal-containing components into the aqueous phase with little or no hydrocarbon phase undercarry into the aqueous phase. The composition is particularly useful in treating crude oil emulsions, and in removing iron-containing components therefrom.

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## METAL PHASE TRANSFER ADDITIVE COMPOSITION AND METHOD

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### Field of the Invention

The present invention relates to methods and compositions for separating emulsions of hydrocarbons and water, and more particularly relates, in one embodiment, to methods and compositions for transferring metal-containing components to an aqueous phase in an emulsion breaking process.

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### Background of the Invention

In an oil refinery, the desalting of crude oil has been practiced for many years. The crude is usually contaminated from several sources, including, but not necessarily limited to:

15

- Brine contamination in the crude oil as a result of the brine associated with the oil in the ground;
- Minerals, clay, silt, and sand from the formation around the oil well bore; and
- Iron sulfides and iron oxides resulting from pipeline and vessel corrosion during production, transport, and storage.

20

25

Desalting is necessary prior to further processing to remove these salts and other inorganic materials which would otherwise cause fouling in downstream heat exchanger equipment and/or form corrosive salts detrimental to crude oil processing equipment. Effective crude oil desalting can help minimize the effects of these contaminants on the crude unit and downstream operations. Proper desalter operations provide the following benefits to the refiner:

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- Reduced crude unit corrosion.
- Reduced crude preheat system fouling.
- Reduced potential for distillation column damage.
- Reduced energy costs.

- Reduced downstream process and product contamination.

Desalting is the resolution of the natural emulsion of water which accompanies the crude oil by creating another emulsion in which about 5 percent relative wash water is dispersed into the oil using a mix valve. The emulsion mix is directed into a desalter vessel containing a parallel series of electrically charged plates. Under this arrangement, the oil and water emulsion is exposed to the applied electrical field. An induced dipole is formed on each water droplet within the emulsion which causes electrostatic attraction and coalescence of the water droplets into larger and larger droplets. Eventually, the emulsion resolves into two separate phases — the oil phase (top layer) and the water phase (bottom layer). The streams of desalted crude oil and effluent water are separately discharged from the desalter.

The entire desalting process is a continuous flow procedure as opposed to a batch process. Normally, chemical additives are injected before the mix valve to help resolve the oil/water emulsion in addition to the electrostatic coalescence. These additives effectively allow small water droplets to more easily coalesce by lowering the oil/water interfacial tension.

Crude oil which contains a high percent of particulate solids can complicate the desalting process. The particulate solids, by nature, would prefer to transfer to the water phase. However, much of the solids in a crude oil from a field exists in tight water-in-oil emulsions. That is, oil-wetted solids in high concentration in the crude may help form tight oil and water emulsions which are difficult to resolve. These tight emulsions are often referred to as "rag" and may exist as a layer between the separated oil and water phases. The rag layer inside the desalter vessel may grow to such an extent that some of it will be inadvertently discharged with the water phase. This is a problem for the waste water treatment plant since the rag layer still contains a high percentage of unresolved emulsified oil.

As mentioned, much of the solids encountered during crude oil desalting consists of iron, most commonly as particulate iron such as iron oxide, iron sulfide, etc. Some of the metals, including iron, may be present in a soluble form. The metals may be present in inorganic or organic forms. In addition to complicating the desalter

operation, iron and other metals are of particular concern to further downstream processing. This includes the coking operation since iron and other metals remaining in the processed hydrocarbon yields a lower grade of coke. Removing the metals from the crude oil early in the hydrocarbon processing stages is desired to eventually yield high quality coke as well as to limit corrosion and fouling processing problems. Several treatment approaches have been made to reduce total iron levels and these all center on the removal of iron at the desalter unit.

It would thus be desirable to develop a composition and method employing it which would cause most or all of the metal-containing components in the crude oil to transfer from the oil phase in a desalter operation, with little or no oil carryunder in the aqueous phase. Nonyl phenol resins have been used as desalting additives in the past, but these materials have come under suspicion as possible hormonal mimics.

#### Summary of the Invention

Accordingly, it is an object of the present invention to provide a composition and method of using it which would transfer a large part of the metal-containing components in the crude oil to the aqueous phase in a desalter operation.

It is another object of the present invention to provide a composition and method for transferring metal-containing components from a hydrocarbon into an aqueous phase in an emulsion breaking operation without causing oil undercarry into the aqueous phase.

Yet another object of the invention is to provide a method and composition to transfer metal-containing components out of a hydrocarbon phase without the use of nonyl phenol resins.

In carrying out these and other objects of the invention, there is provided, in one form, a method of transferring metal-containing components from a hydrocarbon phase to a water phase by adding to an emulsion of hydrocarbon and water an effective amount of a composition. The composition includes at least two of the following components: a diepoxide polymer; a polyol; and an acid selected from the

group of sulfonic acids and carboxylic acids. An aromatic solvent may also be present.

### Detailed Description of the Invention

5 It has been discovered that application to the crude oil of a blend of polymers (surfactants) helps ensure the metal-containing components will largely transfer to the aqueous phase when the emulsion is broken, without causing oil undercarry. More particularly, in one embodiment, the blend includes high molecular weight polyglycol and polymerized polyols from diepoxide, additionally with the presence of a small  
10 amount of an aromatic sulfonic acid. In another embodiment, the blend contains at least two of these three components: a diepoxide polymer; a polyol; and an acid. The acid may be a sulfonic acid and/or a carboxylic acid. Some prior methods teach removing iron from the crude oil, but the problem of oil undercarry in the discharge water usually results.

15 The composition and method of this invention enables rapid penetration through the oil layer around a droplet or particle. This penetration is vividly demonstrated by rapid visual indication of the emulsion breaking.

The composition and method of the invention will be valuable to produce high quality (*i.e.*, high purity) coke from crude which may originally contain high  
20 concentrations of metals and solids, in particular, iron-based solids. Further, the invention advances the technology by removing inorganic material, such as iron, from the crude oil without discharging any oil or emulsion to the waste treatment plant.

In this invention, it will be understood that the term "metal-containing component" includes, but is not necessarily limited to, inorganic species, such as  
25 elemental metal, metal oxides, *e.g.* iron oxides, but also organic metal-containing species, such as iron porphyrin, naphthenate salts of iron, and any other metal-containing material, compound or chemical. These metal-containing components may be in particulate or solid form, or in solubilized form. It will be further understood that while iron is often mentioned as the metal element removed by the compositions  
30 and methods of this invention, that the invention is not limited to iron removal, but is

expected to be useful to remove other metals, such as nickel and vanadium, in a further non-limiting embodiment. Nickel and vanadium are known poisons for catalysts used in fluid catalytic cracking units (FCCUs) downstream.

5 In one embodiment of the invention, the composition of the invention is a blend of at least two of a diepoxide polymer, a polyol, and an acid. In one preferred embodiment of the invention, the diepoxide polymer is one of the components. In an alternate embodiment of the invention, the composition is a diepoxide polymer and a polyol, in the absence of a sulfonic acid and/or a carboxylic acid. In one preferred  
10 embodiment of the invention, all three are employed. In another, non-limiting embodiment, the proportion of these three components may be diepoxide polymer in the range of from about 5 to about 99.8 wt.%, a polyol in the range of from about 0.1 to about 75 wt.%, and an aromatic sulfonic acid in the range of from about 0.1 to about 20 wt.%. In a non-limiting, preferred embodiment of the invention, the proportion of these three components may be diepoxide polymer in the range of from  
15 about 10 to about 85 wt.%, a polyol in the range of from about 1 to about 60 wt.%, and an aromatic sulfonic acid in the range of from about 0.1 to about 15 wt.%. In embodiments where no acid is used, the proportions of diepoxide polymer and polyol are the same as given above.

20 In still another embodiment of the invention, the composition has an absence of ammonium ion and/or an absence of an alkoxylated formaldehyde resin.

By the term "diepoxide polymer" is meant any diepoxide reaction product with a polyol. It will be appreciated that the recitation of "a diepoxide polymer" includes the possibility of more than one diepoxide polymer. The diepoxide polymer may have a molecular weight in the range from about 15,000 to about 30,000. It will  
25 be understood that all molecular weights expressed herein are number average molecular weights. Preferably, the diepoxide polymer may have a molecular weight in the range from about 20,000 to about 25,000. In one non-limiting embodiment of the invention, the diepoxide polymers are reaction products of polyols with glycidyl ethers from a compound containing at least one phenolic group. Non-limiting  
30 examples of suitable diepoxide polymer include, but are not necessarily limited to,

reaction products of bisphenol-A diglycidyl ethers or copolymers of bisphenol-A and epichlorohydrin or Epon 828 with polyols, and the like. The polyols may be made by alkoxyating initiators with alkoxides such as ethylene oxide (EO), propylene oxide (PO), butylene oxide and mixtures thereof. Suitable initiators or starting materials for the polyols include, but are not necessarily limited to, glycerine; trimethylolpropane (TMP); ethylene glycol, propylene glycol, 1,4-butanediol, 1,6-hexanediol, and other glycols; pentaerythritol; sugars and sugar derivatives such as sorbitol or sorbate; amines such as diethylenetriamine, triethylenepentamine, polyethylene(imine) and polyallylamine; and the like. Specific, non-limiting examples of suitable diepoxide polymers include, but are not necessarily limited to, EPON 828 reaction products with polypropylene glycol (PPG).

The polyol may have a molecular weight in the range from about 10,000 to about 60,000. Preferably, the polyol may have a molecular weight in the range from about 11,000 to about 28,000. It will be appreciated that the recitation of "a polyol" includes the possibility of more than one polyol. Specific, non-limiting examples of suitable polyols include, but are not necessarily limited to, those polyols discussed above with respect to the diepoxide polymers.

It will be appreciated that the recitation of "an acid" includes the possibility of more than one sulfonic and/or carboxylic acid. Specific, non-limiting examples of suitable diepoxide polymers include, but are not necessarily limited to, dodecyl benzene sulfonic acid (DDBSA), naphthalene sulfonic acid, dialkylbenzene sulfonic acid, isopropyl sulfonic acid (IPSA); alkylsulfonic acids such as decanesulfonic acid; carboxylic acids such as citric acid and erythorbic acid (*d*-erythro-ascorbic acid, isoascorbic acid); and the like. It will be appreciated that the term "carboxylic acid" also encompasses dicarboxylic acids herein.

The additive blend of this invention is injected into the flowing crude oil before the mix valve in neat form or diluted in a suitable aromatic solvent at a rate to provide effective oil/water separation. Specific, non-limiting examples of suitable aromatic solvents include, but are not necessarily limited to, heavy aromatic solvent, ethyl benzene, xylene, toluene, heavy aromatic naphthalene such as Panasol AN-3N,



FAS 150, EXXON 150, and the like. The amount of solvent used may range from about 10 to about 95 wt.%, based on the total blend with the other three components, preferably from about 20 to about 10 wt.%.

5 The concentration of the additive blend composition of this invention to be used in the crude oil to be effective is very difficult to predict in advance since it depends on multiple, interrelated factors including, but not limited to, the composition of the crude, the desalting conditions (temperature, pressure, etc.), the flow rate of the crude and its residence time in the desalter, among others. Nevertheless, for the purposes of non-limiting illustration, the proportion of the active blend that may be  
10 used in the crude (not including any aromatic solvent) may range from 1 to 500 ppm-w. A preferable concentration will range from 10 to 100 ppm-w.

It is most preferred, of course, that in the practice of this invention there be no oil carryunder in the aqueous phase is minimized. Further, while it is preferred that all of the metal-containing components transfer to the aqueous phase, in one non-limiting  
15 theory of the invention, some of the metals may be transferred from the oil phase into the rag. This proportion of metals is then removed when the rag is cleaned out.

It is also most preferred, of course, that in the practice of this invention all of the metal-containing components transfer to the aqueous phase. In another non-limiting embodiment of the invention, 25% or less metal-containing component is  
20 present in the hydrocarbon phase after desalting, preferably 20% or less metal-containing component remains, most preferably only 10% or less remains.

The invention will be illustrated further with reference to the following Examples, which are not intended to limit the invention, but instead illuminate it further.

25 The following Electrostatic Desalting Dehydration Apparatus (EDDA) Test Method was employed to screen possible blend compositions. The EDDA is a laboratory test device to simulate the desalting process.

30

#### EDDA Test Method

1. Add 800, 600 or 400 ml of crude oil to be tested minus the percent of wash water (depending on the number of tubes the EDDA will hold) to a Waring blender.
2. Add the required percentage of wash water to the blender to bring the total volume up to 800, 600 or 400 ml.
- 5 3. Mix at 50% speed (on the Variac) for 30 seconds. The speed can be reduced if the  $\square$ P on the mix valve is low.
4. Pour the mixture into the EDDA tubes to just below the 100 ml line.
5. Place the tubes in the EDDA heating block that is at the desired test temperature (99°C).
- 10 6. Add the desired quantity of demulsifier, in ppm, to each tube. With every test, a blank must be run for comparison purposes.
7. Place the screw top electrode in the tubes and allow the samples to heat for approximately 15 minutes.
8. Tighten the caps and shake each tube 100-200 times and place back in the heating  
15 block to reheat for five minutes.
9. Place the electrode cover over the tubes and lock into place. Make sure that there is good contact between the cover and the electrode caps.
10. Set the time for five minutes and run at 1500-3000 volts, depending on the test requirements.
- 20 11. At the end of the five minutes, pull the tubes out and check for the percent water drop. Also check the quality of the interface and the quality of the water and record it.
12. Repeat steps 9, 10, and 11 until the desired total residence time is achieved.
13. Determine the best candidates and run a dehydration test on those samples.  
25 a) Fill the desired number of 12.5 ml centrifuge tubes to the 50% mark with xylene.  
b) Use a glass syringe to pull 5.8 ml of dehydrated crude sample from the desired level in the tube and mix in with the xylene in the centrifuge tubes.  
c) Centrifuge the tubes at 2000 rpm for 4 minutes.

- d) Check for the quantity of water, emulsion, and solids that are present in the bottom of the tube and record.

### Total Iron Test from Crude Oil

5 Equipment:

Analytical balance (0.0000 gr readout)  
Muffle furnace capable of reaching 600°C  
Ceramic crucible and crucible lids  
Platinum-tipped crucible tong

- 10 Extreme temperature gloves (Zetex gloves, asbestos replacement)

Reagents

10% (w) solution of hydrochloric acid  
Deionized water.

15

Procedure

1. Using a glass syringe and cannula (long, wide bore needle), withdraw a 10 ml aliquot from the EDDA desalted crude oil. Abstract the oil at a level in the EDDA tube which is at 70 ml below the surface of the oil.
- 20 2. Eject the 10 ml aliquot oil sample into a preweighed (nearest 0.0001 g) ceramic crucible.
3. Place the crucible with the sample into a muffle furnace and ash the sample starting at room temperature and rising to 550°C, then hold for 5 to 6 hours.
4. Remove the crucible from the oven and place in a desiccator to cool for 1 hour.
- 25 5. After cooling, reweigh the crucible and ash. Subtract the crucible's original weight to obtain the weight of the ash.
6. To the ash, add 1 ml of a 10% (w) solution of hydrochloric acid and wait 5 minutes to dissolve the ash.
7. Dilute the solution with 24 ml of deionized water to the dissolved ash solution for a total of 25 ml and wait 2-3 minutes.
- 30

8. Determine the iron concentration in the aqueous acid solution using a Chemetrics Total Iron procedure (Model FE-10, Kit K-6010) (CHEMet).
- a) Place the CHEMet's tapered tip down in the bottom of the sample crucible cup. Snap the tip by pressing the ampoule against the side of the sample cup. The sample fluid will fill the ampoule and begin to mix with the reagent. A small bubble of inert gas will remain in the ampoule to facilitate mixing.
  - b) Remove the fluid-filled CHEMet from the crucible cup. Mix the contents by inverting it several times allowing the bubble to travel from end to end each time, until the solution is uniform in color.
  - c) Wipe all liquid from the exterior of the CHEMet and wait 2 minutes.
  - d) Use the appropriate comparator to determine the concentration of the iron in the aqueous sample.
9. Convert the aqueous iron concentration to the iron concentration found in the oil sample, using the following conversion formula:

$$[\text{Fe}_{(\text{oil})}] = \frac{[\text{Fe}_{(\text{aq})}] \cdot V_{(\text{aq})}}{V_{(\text{oil})}}$$

- where  $[\text{Fe}_{(\text{oil})}]$  = iron concentration in oil, expressed as mg Fe/l  
 $[\text{Fe}_{(\text{aq})}]$  = iron concentration in ash's acidic aqueous solution, in mg Fe/l  
 $V_{(\text{aq})}$  = volume of acidic acid solution in iron Chemetrics test, in ml  
 $V_{(\text{oil})}$  = volume of oil ashed, in ml

Five gallons of crude oil and one gallon of wash water were received from a refinery in Oklahoma for this iron removal study.

The following formulations were prepared.

FeS<sub>1</sub> Components

A	Propoxylated sorbitol	10.4 wt. %
B	Resin esters	5.0
C	6.0 mole EO adduct nonyl phenol resin	4.6
5	FAS 150 Fina Aromatic Solvent	80.0

FeS<sub>2</sub> Components

A	Propoxylated sorbitol	10.6 wt. %
D	Resin esters	4.5
10	C 6.0 mole EO adduct nonyl phenol resin	3.0
	FAS 150	81.9

FeS<sub>3</sub> Components

	Water	78.0 wt. %
15	Citric acid	2.0
	Calfax 2A1 Sodium salt of naphthalene disulfate	12.5
	Nonyl phenol with 9.5 mole ethylene oxide	81.9

FeS<sub>4</sub> Components

20	A	Propoxylated sorbitol	10 wt. %
	E	Nonylphenol resin ethoxylated with 6 moles of ethylene oxide	16
	B	Resin esters	4
	F	Amylphenol resin	4
25	FAS 150		66

RJ-1 Components

	G	Diepoxide reaction product of EPON 828 with polypropylene glycol	22 wt. %
30	H	Polyglycol	8

	DDBSA	0.5
FAS 150		69.5

RJ-2 Components

5	J	Diepoxide	22 wt. %
	H	Polyglycol	8
		DDBSA	0.5
	FAS 150		69.5

10 RJ-3 Components

	K	Diepoxide reaction product made with EPON 828 and propylene oxide and ethylene oxide	24.0 wt. %
	H	Polyglycol	8
		DDBSA	0.5
15	FAS 150		67.5

Other Compositions:

	PC-18	Experimental demulsifier
	FeS <sub>2</sub> A	Experimental demulsifier
20	BPR27141	Complex blend of resins
	BPR27210	Complex blend of resins
	98BH171	Complex blend of resins

Physical Properties

25 The physical properties of the two most promising blends were as shown below:

FeS<sub>4</sub>

Specific Gravity at 78°F (26°C) = 0.96

pH at 25°C, 10% in 50/50 water/IPA (isopropyl alcohol) = 9.47

30 Flash point, TCC = 145°F (63°C)

RJ-1

Specific Gravity at 83°F (28°C) = 0.95

pH at 25°C, 10% in 50/50 water/IPA = 7.60

5 Flash point, TCC = 149°F (65°C)

Examples 1 through 29 demonstrate the amount of iron left in the oil phase after the EDDA test using the indicated components. In all Examples, 5% wash water was used, except for the Examples of Tables V and VIII, where 3% wash water was used. The test temperature was 98°C (208°F). Ten ml aliquots were removed at each indicated time interval.

TABLE I  
EDDA Test Results

<u>Ex.</u>	<u>Compound</u>	<u>Conc.</u> <u>ppm</u>	<u>Vol.% water returned</u> <u>after indicated no. of minutes</u>			<u>Fe, ppm</u>
			<u>5</u>	<u>10</u>	<u>15</u>	
1	FeS <sub>3</sub>	20	0.2	2	2	4.0
2	FeS <sub>2</sub>	20	0.2	0.5	1	3.0
3	FeS <sub>3</sub> /PC-18	12/3*	1.8	2	3.5	4.0

15 \* Concentrations expressed as ratios are ppm of the first component/ppm of the second component.

TABLE II  
EDDA Test Results

<u>Ex.</u>	<u>Compound</u>	<u>Conc.</u> <u>ppm</u>	<u>Vol.% water returned</u> <u>after indicated no. of minutes</u>			<u>Fe<sup>++</sup>, ppm</u>
			<u>5</u>	<u>10</u>	<u>15</u>	
4	FeS <sub>2</sub> A	20	2.6	3	3	6.0
5	FeS <sub>2</sub> /BPR27141	16/4	3.8	4	4	5.0

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6	FeS <sub>3</sub> /BPR27141	16/4	3.5	4	4	5.0
7	Blank	-	-	-	-	7.0

TABLE III

EDDA Test Results

<u>Ex.</u>	<u>Compound</u>	<u>Conc.</u> <u>ppm</u>	<u>Vol.% water returned</u> <u>after indicated no. of minutes</u>			<u>Fe<sup>++</sup>, ppm</u>
			<u>5</u>	<u>10</u>	<u>15</u>	
8	Experimental demulsifier	20	0	0	0	4.5
9	Experimental demulsifier	20	0	0	0	4.5
10	BPR27210/BPR27141	16/3	0.7	1.5	1.7	5.0

5

TABLE IV

EDDA Test Results

<u>Ex.</u>	<u>Compound</u>	<u>Conc.</u> <u>ppm</u>	<u>Vol.% water returned</u> <u>after indicated no. of minutes</u>			<u>Fe<sup>++</sup>, ppm</u>
			<u>5</u>	<u>10</u>	<u>15</u>	
11	FeS <sub>4</sub>	10	2	2.0	3	3.0
12	FeS <sub>1</sub>	20	1.5	1.8	2	6.0
13	BPR27141/B PR27210	4/8	2.4	2.8	3	5.0

TABLE V

EDDA Test Results

<u>Ex.</u>	<u>Compound</u>	<u>Conc.</u> <u>ppm</u>	<u>Vol.% water returned</u> <u>after indicated no. of minutes</u>				<u>Fe<sup>++</sup>, ppm</u>
			<u>5</u>	<u>10</u>	<u>15</u>	<u>18</u>	
14	FeS <sub>4</sub> /RJ-1	16/4	1.2	2	2	2.2	4.0



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15	FeS <sub>1</sub> /RJ-2	16/4	0.5	1.5	1.9	2.0	6.0
16	FeS <sub>1</sub> /RJ-3	16/4	0.5	1.5	1.7	2.0	4.0

TABLE VI  
EDDA Test Results

Ex.	Compound	Conc. ppm	Vol.% water returned after indicated no. of minutes			Fe <sup>++</sup> , ppm
			5	10	15	
17	98BH171/FeS	4/16	3.5	5	5	8.0
18	RJ-1/FeS <sub>4</sub>	4/16	2.0	4	4	4.0
19	RJ-2/FeS <sub>4</sub>	4/16	2	3.5	4	1.0

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TABLE VII  
EDDA Test Results

Ex.	Compound	Conc. ppm	Vol.% water returned after indicated no. of minutes			Fe <sup>++</sup> , ppm
			5	10	15	
20	FeS <sub>4</sub> /RJ-1	16/4	3	3.5	4	1.0
21	FeS <sub>4</sub> /RJ-2	16/4	2.6	3	3.8	2.0
22	FeS <sub>4</sub> /RJ-3	16/4	3	3.5	4	4.0

TABLE VIII  
EDDA Test Results

Ex.	Compound	Conc. ppm	Vol.% water returned after indicated no. of minutes			Fe <sup>++</sup> , ppm
			5	10	15	
23	FeS <sub>4</sub> /RJ-1	16/4	0.5	0.9	1.5	2
24	FeS <sub>4</sub> /RJ-2	16/4	0.5	0.8	1.2	3
25	FeS <sub>4</sub> /RJ-3	16/4	0.5	0.9	1.5	4

TABLE IX  
EDDA Test Results

<u>Ex.</u>	<u>Compound</u>	<u>Conc.</u> <u>ppm</u>	<u>Vol. % water returned</u> <u>after indicated no. of minutes</u>				<u>Fe<sup>++</sup></u> , <u>ppm</u>
			<u>5</u>	<u>10</u>	<u>15</u>	<u>20</u>	
26	FeS <sub>4</sub> /RJ-1	16/4	0.5	2	2.6	3	2
27	FeS <sub>4</sub> /RJ-1	16/6	1.0	2	2.8	3	1
28	FeS <sub>4</sub> /RJ-1	16/8	1.0	2	3	3.5	1
29	FeS <sub>4</sub> /RJ-1	16/10	1.5	2.6	3	3.5	1.5

5 It may be seen that the blend of FeS<sub>4</sub>/RJ-1 gives the best results as shown by values of 1 and 2 ppm iron retained in Examples such as 20, 23, and 26 through 28. Because of the promise of RJ-1 in the laboratory tests, it was used alone in a field trial in Oklahoma. The iron measurements were made using an atomic adsorption method, and are shown in Tables X and XI for the indicated time periods.

10

TABLE X  
Example 30 — Field Trial of RJ-1 Alone

<u>Date</u>	<u>Raw Crude Fe, ppm</u>	<u>Desalter Effluent Fe, ppm</u>	<u>Resid Fe, (Feed to Coker), ppm</u>
11/28	19	15	90
11/29	16	14	79
11/30	18	16	76
12/1*	19	37	173
12/2	19	11	49
12/3	-	-	-
12/4	17	13	49

\* From 9:00 p.m. 11/30 to 5:00 a.m. 12/1, tank bottoms slop was being injected into the desalter which caused the high Fe values on this day.

TABLE XI

Example 30 — Field Trial of RJ-1 Alone

<u>Date</u>	<u>Time</u>	Raw Crude <u>Fe. ppm</u>	Resid Fe, (Feed to <u>Coker</u> ), ppm	Comments
1/25	900	16	81	
1/26	900	19	98	
1/27	1700	20	54	Trial with RJ-1 starts
1/28	1500	19	67	
1/29	800	22	74	Mud washed for 4+ hours
2/1	900	—	49	
2/2	900	17	46	
2/3	1300	15	66	
2/4	900	17	50	
2/5	800	19	—	
2/5	1600	20	40	Rag sample = 680 ppm, Fe
2/8	1500	23	56	
2/9	800	22	56	
2/9	1400	21	52	
2/10	800	18	63	
2/11	900	17	42	
2/11	1530	11	42	
2/12	800	14	46	
2/13	800	23	69	
2/15	800	24	37	
2/16	1000	16	38	
2/17	900	15	41	
2/18	900	16	65	
2/19	900	23	80	Excessive mudwash before sample obtained

2/22	900	8	31
2/22	1600	12	33
2/23	900	11	22

In the foregoing specification, the invention has been described with reference to specific embodiments thereof, and has been demonstrated as effective in transferring metal-containing components, *e.g.* iron particulates, from crude oil to the aqueous phase in bench scale desalting testing, as non-limiting examples. However, it will be evident that various modifications and changes can be made thereto without departing from the broader spirit or scope of the invention as set forth in the appended claims. Accordingly, the specification is to be regarded in an illustrative rather than a restrictive sense. For example, specific polyols and diepoxide polymer reaction products, and combinations thereof, other than those specifically tried, falling within the claimed parameters, but not specifically identified or tried in a particular application to transfer metal-containing components into the aqueous phase, are within the scope of this invention. Likewise, aromatic sulfonic acids other than DDBSA are expected to be useful in various polymer blends not explicitly described herein. Similarly, it is expected that the inventive compositions will find utility as metal transfer compositions for other fluids besides crude oil emulsions.

Claims

We Claim:

1. A method of transferring metal-containing components from a hydrocarbon phase to a water phase comprising:  
adding to an emulsion of hydrocarbon and water, an effective amount of a composition to transfer metal-containing components from a hydrocarbon phase to a water phase comprising at least two of the following components:  
a diepoxide polymer;  
a polyol; and  
an acid selected from the group consisting of sulfonic acids and carboxylic acids; and  
resolving the emulsion into hydrocarbon phase and an aqueous phase, where at least a portion of the metal-containing components are transferred to the aqueous phase.
2. The method of claim 1 where in the adding of the composition, the composition comprises a diepoxide polymer and a polyol.
3. The method of claim 1 where in the adding of the composition, the composition comprises a diepoxide polymer.
4. The method of claim 1 where in the adding of the composition, the composition further comprises  
from about 5 to about 99.8 wt.% diepoxide polymer;  
from about 0.1 to about 75 wt.% polyol; and  
from about 0.1 to about 20 wt.% acid.

5. The method of claim 1 where in the adding of the composition, the diepoxide polymer has a molecular weight in the range from about 15,000 to about 30,000.
6. The method of claim 1 where in the adding of the composition, the polyol has a molecular weight in the range from about 10,000 to about 60,000.
7. The method of claim 1 where in the adding of the composition, the composition further comprises an aromatic solvent.
8. The method of claim 7 where in the adding of the composition, the composition contains from about 10 to about 95 wt.% aromatic solvent.
9. The method of claim 1 where in the adding of the composition, the amount of the composition added to the emulsion is at least 1 ppm.
10. A composition for transferring metal-containing components from a hydrocarbon phase to a water phase comprising at least two of the following components:
  - a diepoxide polymer;
  - a polyol; and
  - an acid selected from the group consisting of sulfonic acids and carboxylic acids.
11. The composition of claim 10 where two of the components are a diepoxide polymer and a polyol.
12. The composition of claim 10 where at least one of the components is a diepoxide polymer.
13. The composition of claim 10 where the composition further comprises

from about 5 to about 99.8 wt.% diepoxide polymer;  
from about 0.1 to about 75 wt.% polyol; and  
from about 0.1 to about 20 wt.% acid.

14. The composition of claim 10 where the diepoxide polymer has a molecular weight in the range from about 15,000 to about 30,000.
15. The composition of claim 10 where the polyol has a molecular weight in the range from about 10,000 to about 60,000.
16. The composition of claim 10 where the composition further comprises an aromatic solvent.
17. The composition of claim 16 where the composition contains from about 10 to about 95 wt.% aromatic solvent.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/05845

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : Please See Extra Sheet.  
US CL : 208/187, 188, 189, 252; 516/160, 190, 193  
According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 208/187, 188, 189, 252; 516/160, 190, 193

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST

search terms: emulsion\$, diepoxide\$, polyol\$, sulSonic\$, carboxylic\$

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,551,239 A (MERCHANT ET AL) 05 November 1985 (05/11/85), see abstract, column 3, lines 40-45 and 60-65, and column 5, lines 48-50.	1, 6, 9, 10, 15
X	US 4,737,265 A (MERCHANT, JR. ET AL) 12 April 1988 (12/04/88), see abstract, column 3, lines 24-28, 39-45 and 53-56 and column 5, lines 50-53.	1, 9, 10
X	US 5,667,727 A (BREEN ET AL) 16 September 1997 (16/09/97), see abstract, column 2, lines 60-64, column 3, lines 54-57 and column 5, lines 35-40.	1, 2, 3, 5, 9, 10, 11, 12, 14

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier document published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"Z" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

21 MAY 2000

Date of mailing of the international search report

12 JUN 2000

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## INTERNATIONAL SEARCH REPORT

International application No.  
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## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	US 5,981,687 A (BREEN ET AL) 09 November 1999 (09/11/99), see abstract, column 2, lines 63-67, column 3, lines 57-62 and column 5, lines 52-54.	1, 2, 3, 5, 9, 10, 11, 12, 14
X — Y	US 5,256,305 A (HART) 26 October 1993 (26/10/93), see column 1, lines 6-12, column 2, lines 66-88 and column 3, lines 3-7.	1, 2, 3, 10, 11, 12 4, 7, 8, 13, 16, 17
Y	US 5,078,858 A (HART ET AL) 07 January 1992 (07/01/92), see column 1, lines 4-6 and 49, and column 2, lines 24-37.	4, 7, 8, 13, 16, 17
A	US 5,446,233 A (LEWIS ET AL) 29 August 1995 (29/08/95), see entire document.	1-17
A	US 4,411,775 A (MCCOY ET AL) 25 October 1983 (25/10/83), see entire document.	1-17
A	US 4,853,109 A (REYNOLDS) 01 August 1989 (01/08/89), see entire document.	1-17
A	US 4,326,968 A (BLAIR, JR.) 27 April 1982 (27/04/82), see entire document.	1-17
A	US 2,792,352 A (GROOTE ET AL) 14 May 1957 (14/05/57), see entire document.	1-17

INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/05845

A. CLASSIFICATION OF SUBJECT MATTER:  
IPC (7):

C10G 17/00, 17/02, 17/04, 27/00, 33/00, 33/04; B01D 17/05; C09K 3/00